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REACTIONS OF STANNYLFURANONES: FACILE PREPARATION OF 4-HALO-2(5H)-FURANONES

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Abstract: 4-Halo-2(5H)-furanones are readily prepared from 4-tributylstannyl-2(5H)-furanone.

We recently required access to 2(5H)-furanones bearing a leaving group at the β-position of the olefin, to enable addition-elimination reactions to occur with either nucleophiles or radicals. The obvious candidates[1] to mediate this transformation, *viz.* 4-halofuranones, are not readily available; indeed, 4-iodo-2(5H)-furanone is not reported in Chemical Abstracts. We deduced that a suitable precursor to these elusive halogeno compounds would be the corresponding (and recently reported) vinyl stannane, 4-tributylstannyl-2(5H)-furanone (1).[2]

Synthetic routes to both 4-chloro- and 4-bromo-2(5H)-furanone (2 and 3, respectively) have been reported;[4,5] the former has been prepared *via* a palladium catalysed carbonylation reaction of propargyl alcohols, as reported by Larock *et al.* [3] These workers found that mercuric chloride reacted with a variety of propargylic alcohols to give (E)–β–chloro–γ-hydroxy vinyl mercuric chlorides which undergo carbonylative insertion reactions in the presence of palladium salts to yield 4-

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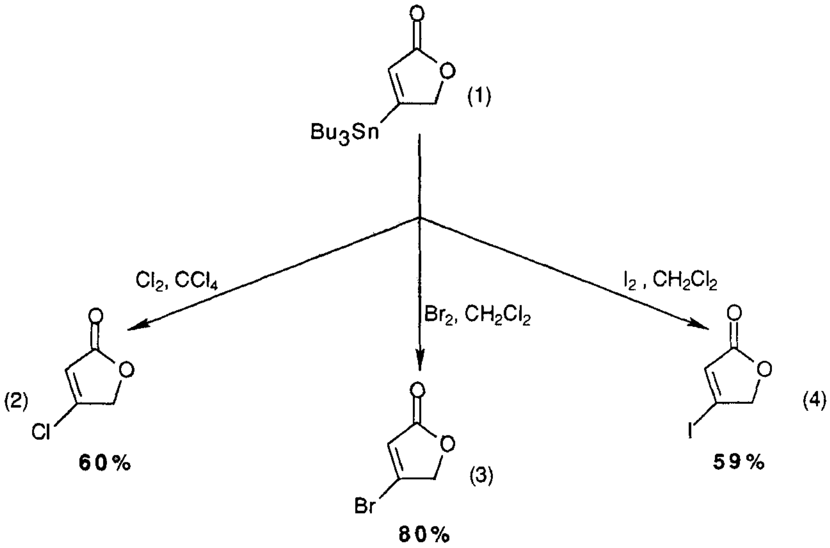
chloro-2(5H)-furanones in moderate overall yield. The bromolactone has been prepared by hydrobromination of 4-hydroxytetrolic acid and subsequent lactonisation.[4] Both these syntheses proceed with moderate overall yield. Neither reaction is reported to be compatible with preparation of iodolactone (4).



We have found that reaction of 4-tributylstannyl-2(5H)-furanone with elemental chlorine, bromine or iodine is an efficient entry to the corresponding halofuranones. Thus, reaction of a carbon tetrachloride solution of chlorine gave a 60 % yield of chlorofuranone (2). This compares with the previously reported yield of 51% (overall).[3] Bromination of (1) occurs upon exposure of the stannane to bromine to give bromofuranone (3) in 80% yield after chromatographic purification. Reaction with elemental iodine proceeds in 59% yield to give iodofuranone (4). These yields are unoptimized. Attempts to fluorinate (1) have so far proved unsuccessful.

4-Chloro-2(5H)-furanone (2) [3]

To a solution of 4-(tributylstannyl)-2(5H)-furanone (182 mg, 0.488 mmol) in carbon tetrachloride (3 ml) was added a solution of chlorine in carbon tetrachloride (0.34 ml of a saturated solution, ~ 1 mmol) and the reaction mixture allowed to stand whilst the progress of the reaction was monitored by t.l.c. To compensate for evaporative losses, an additional 1 mmol of chlorine solution was added to complete the consumption of starting material. To the now colourless solution was added solid KF (250 mg) and the mixture stirred for 1 hour and filtered. The filtrate was washed with aqueous KF solution (8M, 2x5 ml), dried ($MgSO_4$) and evaporated to give the title compound[4] as a colourless gum (34.7 mg, 60%). $\delta_H(CDCl_3)$ 6.1 (1H, t, J=2 Hz, vinylic), 4.8 (2H, d, J=2 Hz, CH_2O).

4-Bromo-2(5H)-furanone (3) [4]

To a stirred solution of 4-(tributylstannyl)-2(5H)-furanone (98 mg, 0.26 mmol) in dichloromethane (3 ml) under a nitrogen atmosphere was added dropwise at room temperature a solution of bromine (0.02 ml, 0.39 mmol) in dichloromethane (2 ml). After stirring at room temperature for 3 hours t.l.c. indicated the complete consumption of starting material. Solid KF (150 mg) was added and the mixture stirred for 1 hour. Subsequent filtration, evaporation and column chromatography of the residue (eluent: ether-petroleum ether [1:3]) afforded 4-bromo-2(5H)-furanone[5] as a colourless crystalline solid (34.3 mg, 80%); $\delta_H(CDCl_3)$ 6.35 (1H, t, J=1.84 Hz, vinylic) 4.86 (2H, d, J=1.84 Hz, CH_2O).

4-Iodo-2(5H)-furanone (4)

To a solution of 4-(tributylstannyl)-2(5H)-furanone (74 mg, 0.198 mmol) in dichloromethane (5 ml) was added iodine (75 mg, 0.298 mmol). The resulting purple solution was stirred at room temperature for 20 hours after which time reaction was complete as indicated by disappearance of starting materials as evinced by t.l.c. Solid KF (115 mg) was added and the mixture stirred for three hours. Subsequent filtration, evaporation and column chromatography (eluent: ether - petroleum ether [1:3]) afforded 4-iodo-2(5H)-furanone as a colourless crystalline solid (24.5 mg, 59%, m.pt. 101-102°C);

IR; υ_{max} 2955, 2867, 1787(C=O), 1743(C=O), 1594(C=C), 1139, 1010 cm^{-1};
^1H nmr (TMS/$CDCl_3$) δ = 6.57 (1H, t, J=2.01 Hz, vinylic), 4.85 (2H, d, J=2.01 Hz, CH_2O);
^{13}C nmr (TMS/$CDCl_3$) δ = 171.2, 129.4, 118.1, 78.8;
MS; m/z=M^+ 210(100%), 83, 39; Found M^+=209.9187, $C_4H_3O_2I$ requires 209.9180
Anal. Calc.:22.88% C, 1.44% H; Found: 23.18% C, 1.52% H.

Acknowledgement

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